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HIGH PERFORMANCE "M5" FIBER FOR BALLISTICS / STRUCTURAL COMPOSITES

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ABSTRACT

The ballistic impact potential of M5 fiber-based armor systems is estimated using an "armor materials by design" model for personnel armor; the model is based on a dimensional analysis of the mechanical properties of the fibers used to construct the armor system. The model indicates that M5 fiber-based armor has the potential to substantially decrease the weight of body armor while enhancing or maintaining impact performance. Composite fragmentation armor systems were developed using less than optimal quality M5 fiber and tested under ballistic impact; the performance of these armor systems was exceptional.

1. INTRODUCTION

M5 fiber is a high performance fiber originally developed by Akzo Nobel (Brew et al, 1999; van der Jagt and Beukers, 1999; Sikkema, 1999; Lammers et al, 1998; Klop and Lammers, 1998; and Hageman et al, 1999) and currently produced by Magellan Systems International (Magellan). This work describes the potential of M5 as an armor material and illustrates that potential by examining the ballistic impact response of composite materials which contain less than optimal M5 fiber from the early stages of the fiber's development.

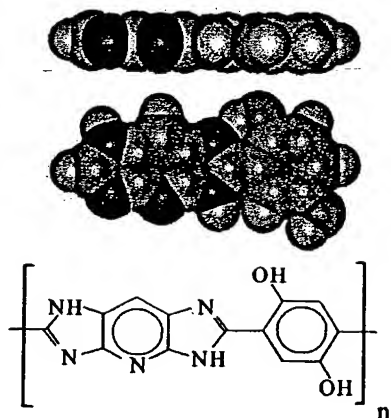


Fig. 1. M5 polymer repeat unit.

M5 fiber is based on the rigid-rod polymer poly{diimidazo pyridinylene (dihydroxy) phenylene}; the polymer repeat unit is illustrated in Figure 1. The crystal structure of M5 is different from all other high strength fibers; the fiber features typical covalent bonding in the main chain direction, but it also features a hydrogen bonded network in the lateral dimensions [Klop and Lammers, 1998]. M5 fibers currently have an average modulus of 310 GPa, (i.e. substantially higher than 95% of the carbon fibers sold), and average tenacities currently higher than aramids (such as Kevlar or Twaron) and on a par with PBO fibers (such as Zylon), at up to 5.8 GPa.

The first composite test bars that were tested for axial compressive strength confirmed the high compressive properties of the fiber in composite form, with onset of plastic deformation being found at stress levels up to 1.7 GPa in 3- and 4-point bending tests [van der Jagt and Beukers, 1999]. This result confirms the theoretical relation, which predicts that for well-oriented polymer fibers the compressive strength is about 0.3 times the interchain shear modulus. Northolt [Northolt and Baltussen, 2001] gives the following relationship for compressive yield stress in polymer fibers:

$$0.23g < \sigma_{yc} < 0.41g \quad (1)$$

where g is the shear modulus ($g=5.9$ GPa for heat treated M5 fibers [Northolt and Baltussen, 2001]), indicating that M5 compressive properties are expected to be on par with the compressive strength of PAN-based carbon fibers.

An ideal fiber for ballistic protective equipment would be affordable and possess properties that make it an attractive fiber for multiple applications. That is, since the demand for ballistic protective materials is relatively small compared to the demand for affordable high performance structural composite materials, the economies of scale resulting from serving multiple markets should make the fiber more viable.

With respect to mechanical properties, such a fiber should possess a high tensile and compressive modulus, high tensile and compressive strength, high damage tolerance, low specific weight, good adhesion to matrix materials (for structural composites) and a good temperature resistance. Up until the discovery of M5, no single fiber has existed with all of these advanced properties in one molecular structure.

The M5 fiber used in this work was produced by Magellan using a batch process on bench-scale equipment. The bench scale equipment used in this work had several limitations. Problems associated with the inability to effectively de-gas the polymer dope prior to spinning created a situation where air bubbles had formed upstream of the spinneret. Figure 2 is a photograph of an air bubble which had formed over one of the spinneret holes.

The fibers produced for this work were washed on bobbins with no tension and heat treatment was performed with low tension. These problems lead to fibers with less than optimal crystal orientation, and hence less than optimal ultimate mechanical properties (e.g. average fiber strength was 4 GPa). Recently completed modifications to the bench-scale spin line to rectify these problems have already resulted in substantially increased fiber mechanical properties (e.g. single fiber strength of 7.2 GPa has already been observed), These are expected to correspondingly increase ballistic impact performance.



Fig. 2. Air bubble formed at spinneret

Despite the fact that the ultimate mechanical properties of the available M5 fibers were lower than we would have estimated to be required in order for the fiber to be a viable high performance ballistic protective material, it was decided to conduct ballistic impact tests to determine whether M5 had intrinsic limitations that might make the fiber unsuitable as a ballistic protective material.

2. M5 MECHANICAL PROPERTIES

Approximately 1 kg of moderate-quality M5 fiber was used in this work; the average mechanical properties of single fibers which were tested at a gage length of 10 cm are listed in Table 1.

Table 1: Average M5 Mechanical Properties of 10 cm Gage Length Fibers (as of 2000)

Tensile Modulus (GPa)	271
Tensile Strength (MPa)	3960
Elongation at Break (%)	1.4
Density (g/cm ³)	1.7

The strength of the fibers tested as part of this work is low compared to the goal mechanical properties for M5. The strength was low even when compared to the best available fibers currently in production; fiber properties are continually increasing with advances in processing of the fiber. Recently, M5 fibers with tensile strength of up to 7.2 GPa and tensile modulus of 344 GPa have been observed. The current best available strength is nearly twice the strength and 25% more stiff than the fiber used as part of this work, despite the fact that these improved fibers were obtained using fiber produced from the same bench-scale batch-process that was used to produce the earlier fiber.

M5 fibers investigated as part of this work were observed to be stable after exposure to visible and ultraviolet light. After exposure to Zenon lamp for up to 100 hours, the M5 fibers retained essentially all of the virgin fiber strength; by comparison, Zylon fibers lost over 35% of the virgin fiber strength at this exposure time.

The M5 yarns were similarly stable after exposure to elevated temperature and humidity, as illustrated in Figure 3. After exposure to 180 F and 85% relative humidity (RH) for up to 11 weeks, the M5 yarns retained essentially all of the virgin fiber strength; Zylon yarns lost over 20% of the virgin strength at this exposure time. The scatter in the data for M5 strength loss of Figure 3 is attributed to the (large) defect frequency in the fiber due to previously mentioned processing conditions; scatter in the data for fibers exposed to light was even larger than for the yarns illustrated in Figure 3.

Elemental analysis of the M5 fibers indicated that the fibers contained 0.11% phosphorus by weight; Zylon

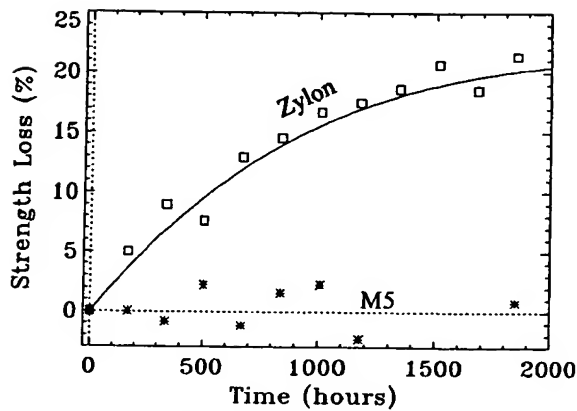


Fig. 3. Strength loss in M5 and Zylon after exposure to 180F, 85% R.H.

fibers, spun from the same solvent (polyphosphoric acid), were found to contain 0.34% phosphorus. The connection between reduced acid content and poor hot/wet performance is not clear.

Fibers fractured under quasi-static tensile stress showed a highly fibrillated fracture morphology, as illustrated in Figure 4. The extensive axial splitting of the fibers is typical of the fibers observed in this work.

Recent fiber physics theory, as proposed by Northolt and Baltussen, 2001, has also been used to project the target mechanical properties for M5. This theory allows for the prediction of target mechanical properties for any high strength fiber, and is based on both empirical data and observation of a large number of high strength fibers, including aramids, PBO, and others. The goal mechanical properties of M5 are presented in Table 2.

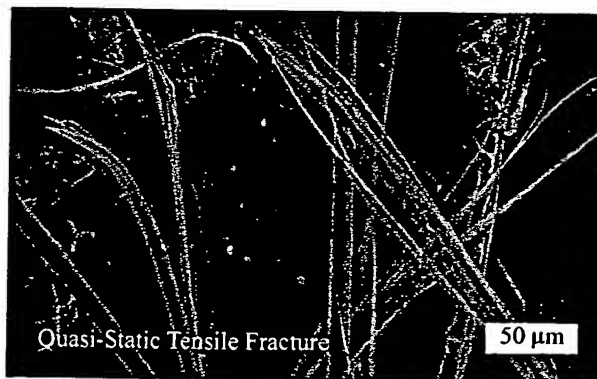


Fig. 4. ESEM micrographs of quasi-static tensile fracture in M5 fibers showing extensive axial cracking of the fiber.

Table 2: M5 Goal Mechanical Properties

Property	
Tensile Modulus (GPa)	450
Tensile Strength (GPa)	9.5
Elongation at Break (%)	2.0 - 2.5
Density (g/cm ³)	1.7

3. ARMOR PERFORMANCE MODEL

A set of dimensionless parameters for the optimization of textile-based body armor systems, which provide critical guidance to fiber developers, body armor system material integrators, and body armor system designers for the continuous product improvement of personnel armor items was previously described by Cunniff, 1999. The dimensionless parameters allow for directed optimization of textile fibers based on an objective assessment of the trade-off in ballistic performance associated with altering a fiber's mechanical properties.

In the dimensional analysis, it is assumed that fiber specific toughness and fiber strain wave velocity are the only essential mechanical properties of the system, and that presented area and mass are the only essential characteristics of the projectile. It is further assumed the fiber is linearly elastic so that the product of ultimate strength and elongation at break determine the fiber toughness; fiber strain wave velocity is taken to be the square root of the specific tensile modulus. The objective of the analysis is to relate these system and projectile characteristics to the principal design parameters of an armor system, namely V50 velocity (the velocity where impacting projectiles are expected to defeat a system 50% of the time) and armor system areal density (weight per unit area). The dimensional ratios for a textile-based armor system are given in Equation 2.

Examination of Equation 2 indicates the dimensionless parameters relate ballistic impact performance to fiber mechanical properties independent of impacting projectile mass, presented area or armor system areal density (weight per unit area). The first parameter, a dimensionless V50 velocity, is defined as the V50 velocity normalized by the cube root of the product of specific work to break the fiber and the acoustic wave speed in the fiber. The second dimensionless parameter relates to the armor system configuration and penetrator and is defined

as the product of the system areal density (A_d) and projectile presented area (A_p) divided by the projectile mass (m_p). Hence, results of the dimensional analysis indicate that a single curve may be used to relate the V50 performance of any armor system material to any penetrator, independent of the system areal density.

$$\Phi\left(\frac{V_{50}}{(U^*)^{1/3}}, \frac{A_d A_p}{m_p}\right) = 0 \quad (2)$$

- σ - Fiber ultimate axial tensile strength
- ϵ - Fiber ultimate tensile strain
- ρ - Fiber density
- E - Fiber modulus (assumed linearly elastic)
- A_p - Projectile presented area
- m_p - Projectile mass
- V_{50} - V50 ballistic limit
- A_d - System areal density
- U^* - the product of fiber specific toughness and

$$\text{strain wave velocity } U^* = \frac{\sigma \epsilon}{2\rho} \sqrt{\frac{E}{\rho}}$$

Archival data for the V50 ballistic limit of several hundred different V50 tests was used in this work. System areal densities ranged from 0.27 g/cm² (8.9 oz/ft²) to 2.5 g/cm² (81 oz/ft²). Projectiles had a length-to-diameter ratio of approximately one; they were either steel or tungsten with mass of 2-, 4-, 16- 64-or 128-grain (0.12, 0.26, 1.0, 4.1, or 8.2-g). Material types included Kevlar 29®, Kevlar 129®, Kevlar 49®, Kevlar KM2®, heavy tow carbon fiber, E-glass, poly(p-phenylene benzobisoxazole) (PBO obtained from Dow Chemical Co., and from Toyobo under the trade name Zylon®), nylon 6,6, and Spectra 1000® fabrics. Composite materials investigated were Zylon unidirectionals with a thermoplastic resin, Kevlar® 29/poly(vinyl-butylal)/phenolic, Kevlar® KM2/poly(vinyl-butylal)/phenolic, Spectra 900 fabric/vinylester, SPECTRA shield®/Kraton®, E-glass/polyester, carbon fiber / epoxy, and nylon/poly(vinyl-butylal)/phenolic. In each case (with the exception of E-glass and carbon fiber composites) the resin content was approximately 15-18% by weight; the resin content of the glass and carbon composites was approximately 30%.

Broad agreement was shown among the differing armor systems and projectiles, with the notable exception of ultrahigh molecular weight polyethylene (UHMWPE), carbon and glass fibers. UHMWPE systems significantly underperformed expectations, presumably due to fiber melting during the impact event. In the case of UHMWPE, the failure to correlate well with the U^* theory is taken to be an indication that impact performance of high melting point fibers may exceed the performance of equivalent low-melting point fibers.

The results of the dimensional analysis indicate that the principal fiber property of interest is $(U^*)^{1/3}$. Tabulated values for this parameter for a number of armor materials and for M5 are provided in Table 3.

Table 3: Fiber Mechanical Properties

Fiber	Strength (σ) (GPa)	Failure Strain (ϵ) (%)	Modulus (E) (GPa)	$(U^*)^{1/3}$ (m/s)
PBO	5.20	3.10	169	813
Spectra 1000	2.57	3.50	120	801
600 den. Kevlar KM2	3.40	3.55	82.6	682
850 den. Kevlar KM2	3.34	3.80	73.7	681
840 den. Kevlar 129	3.24	3.25	99.1	672
1500 den. Kevlar 29	2.90	3.38	74.4	625
200 den. Kevlar 29	2.97	2.95	91.1	624
1000 den. Kevlar 29	2.87	3.25	78.8	621
1140 den. Kevlar 49	3.04	1.20	120	612
carbon fiber	3.80	1.76	227	593
E-Glass	3500	4.7	74	559
nylon	0.91	N/A	9.57	482
M5 Conservative	8500	2.5	300	940
M5 Goal	9500	2.5	450	1043
M5 (2001 Sample)	3960	1.4	271	583

The dimensional analysis model allows for the estimation of the performance of an armor system based solely on the (quasi-static) mechanical properties of the fibers that constitute the armor system. The results of the dimensional analysis indicate that V50 velocity of an armor systems scales with $(U^*)^{1/3}$; for a fixed target areal density, and a fixed projectile, the ratio of V50 ballistic

limits for two armor systems may be computed by the ratio of the $(U^*)^{1/3}$ numbers.

As illustrated in Figure 5, V50 performance curves for an armor system where data is available may be scaled (by the ratio of the $(U^*)^{1/3}$ numbers) to approximate the performance of a hypothetical armor system. In Figure 5, we approximate the performance of M5 for three possible sets of M5 fiber ultimate mechanical properties; the goal mechanical properties, a conservative estimate of the mechanical properties that may be achieved with M5, and a 15% improvement over the goal mechanical properties. The estimate of performance of the M5 fiber used as part of this work (having mechanical properties as indicated in Table 3) is slightly inferior to the performance of Kevlar 29, as indicated in Table 3.

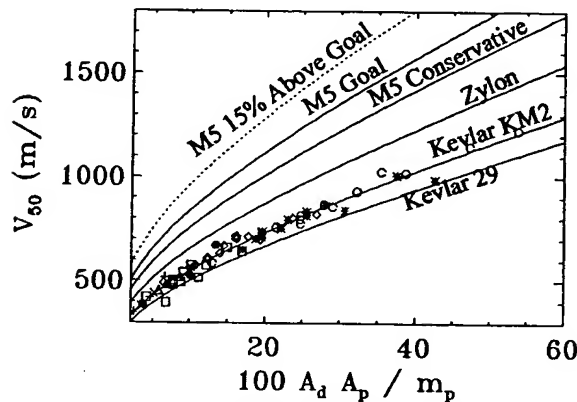


Fig. 5. Expected M5 performance compared to aramids and PBO

Figure 5 may be used to estimate the weight reduction of one armor system over another which will be expected to yield the same ballistic limit. In the case of M5 armor systems, these estimated weight reductions (relative to Kevlar KM2 flexible fragmentation protection) are tabulated in Table 4.

Table 4: Estimated Weight Reduction for Flexible Fragmentation Protection using M5

Armor Material	Percent Weight Reduction
Kevlar KM2	0
Zylon	25
M5 Conservative	42
M5 Goal	55
M5 (15% enhanced mechanism)	63

4. ARMOR SYSTEM DEVELOPMENT

Six-inch wide unidirectional tapes were prepared by fusing non-woven thermoplastic sheet goods onto aligned and spread fibers; a basis weight of 98 g/m² with a resin content of approximately 12 percent was used to prepare the unidirectional tapes. The resin and resin content for this work is similar to that previously successfully used to prepare fragmentation protective Zylon composites. The extremely low resin content (relative to the resin content typically used to prepare structural composites) was selected to optimize ballistic performance over structural rigidity or strength.

The low basis weight (or ply areal density) was selected to optimize ballistic performance. The ply areal density used in this work was constrained by the available areal density of the thermoplastic nonwoven used to fuse the fibers and by the desired resin volume fraction, rather than by the ability to spread the fibers. M5 yarns, which were approximately 860 denier, were found to spread easily. It is estimated that 1500 denier or greater yarns could be used to produce equal areal density unidirectional sheet goods.

Composites were prepared in a two-step process. In the first step, cross-ply unidirectional (0,90) sheet goods were prepared by fusing 4(6"x12") unidirectional plies into 12"x12" lamina. Fusing conditions used for this step were 300 F, 10 psi, 30 seconds. These lamina were further consolidated in a compression molding machine. Processing conditions included a temperature ramp to 300 F at a consolidation pressure of 900 psi, a 30 minute soak at 300 F and 900 psi, and a cooling cycle from 300 to 150 F at 900 psi. Figure 6 is a photograph of the resulting composite panel following ballistic testing. The single nominal 1 lb/ft² panel was used for 3 V50 tests. Shots were confined to the interior of the panel, and no shots were placed in the center region near the seams of the unidirectional tape, as illustrated in Figure 6.

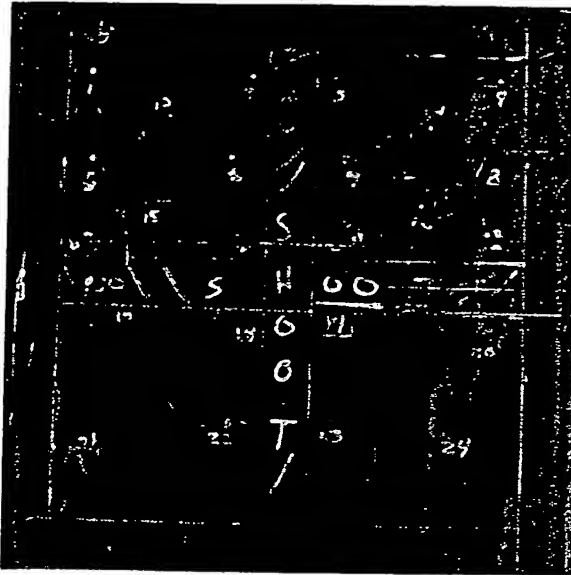


Fig. 6. M5 composite armor panel

5. BALLISTIC TESTING RESULTS

V50 ballistic impact tests were conducted using 2-, 4-, and 16-grain right circular cylindrical steel projectiles. Results of the V50 tests are illustrated in Figure 7. In the Figure, V50 results for M5 composites are compared to similarly prepared Zylon composites. The performance of M5 is seen to be nearly comparable to the Zylon material.

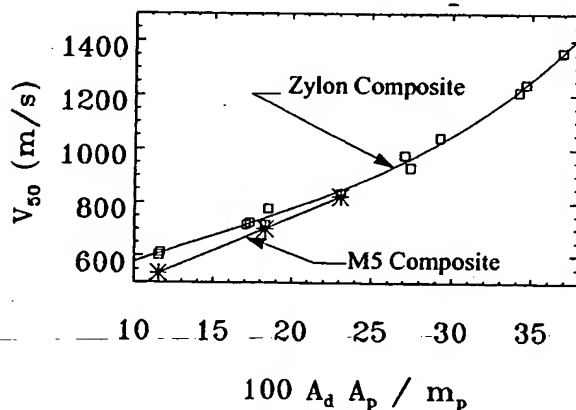


Fig. 7. Results of M5 Ballistic Testing.

The exceptional performance of M5 composites was unexpected; the performance, based on the dimensional analysis model was expected to be slightly inferior to Kevlar 29 composites. Figure 8 is a comparison of the expected and observed impact performance of M5 composites. In the plot, the Zylon data and Zylon performance curve of Figure 8 are scaled by the $(U^*)^{1/3}$

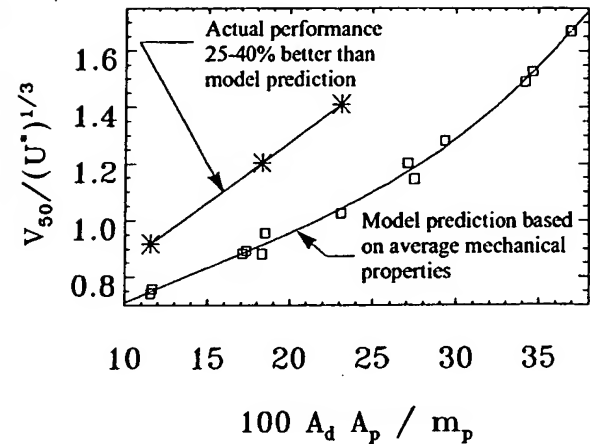


Fig. 8. Estimated M5 fabric ballistic impact performance

number for Zylon. The model indicates that the M5 data (scaled by the $(U^*)^{1/3}$ number for M5) should plot on this same curve; actual V50 performance of M5 composites is seen to be approximately 25 - 40% higher than expected.

Fractured fibers near the impact point within a composite panel showed fibrillated fibers somewhat similar to the quasi-static failure topography, as illustrated

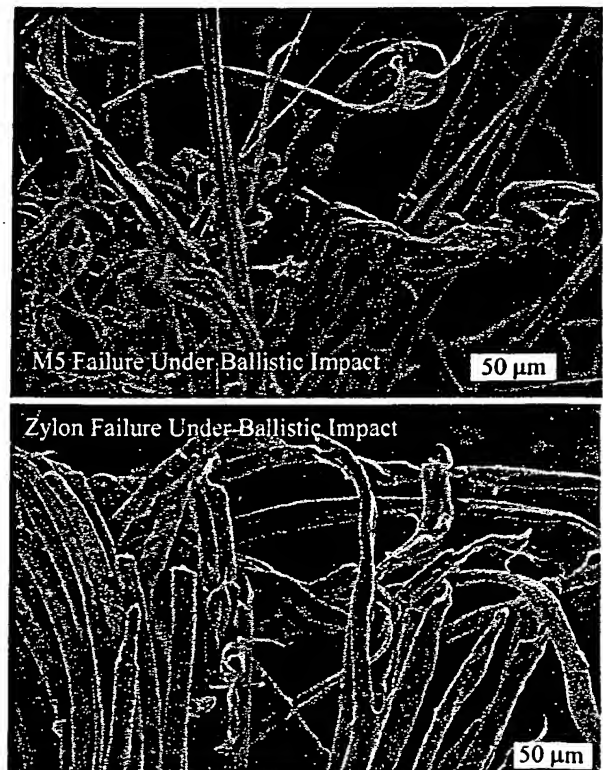


Fig. 9. Fractured M5 and Zylon fibers at the impact point following ballistic impact testing.

in the ESEM micrographs of Figure 9. The fractured fibers showed some evidence of lateral yielding, but yielding of the fibers was much less pronounced for M5 than for Zylon fibers, as illustrated in Figure 9.

Kink band formation, which is frequently observed in aramid and PBO armor systems in post-impact examination of the fibers was also much less pronounced in M5 panels than in similarly constructed Zylon panels. Kink bands (which are indicative of axial compressive failure of the fiber) are thought to result from snap-back of the fibers following tensile failure. Similarly, the axial buckling of some of the M5 fibers seen in Figure 9 is thought to have occurred after these fibers had failed.

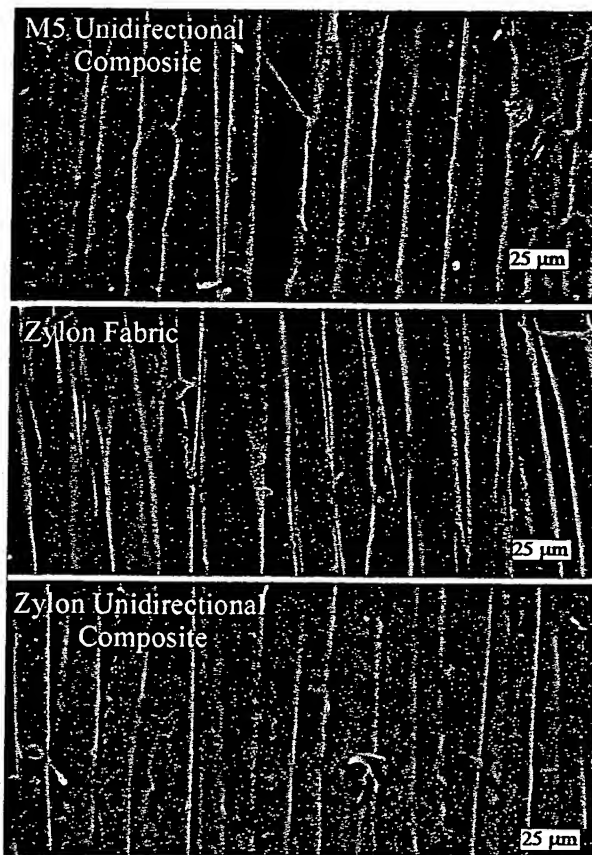


Fig. 10. Lateral yielding of M5 and Zylon fibers in the region immediately under the footprint of the projectile.

Evidence of lateral yielding of the fibers in unperforated plies immediately under the footprint of the projectile was observed to be much less severe in M5 composites than for similarly constructed Zylon composites or for Zylon fabrics, as indicated in Figure 10. Lateral yielding in Zylon fabrics is seen to be more

pronounced than in unidirectional composites. The fibers within the low basis weight unidirectional composites are spread more evenly than the fibers within fabrics and are coated with resin, providing some constraint to lateral yielding.

6. DISCUSSION

In the model, it is assumed that lateral compressive forces on the fibers of a body armor system do not contribute to appreciable energy absorption or to premature failure of the system. Since lateral compressive stresses are quite localized, the former assumption appears to be reasonable while the latter assumption is expected to lead to discrepancies for some materials. Examination of scanning electron micrographs of the region immediately under the impact point in an aramid fabric armor system indicates considerable localized yielding of the fibers; similarly deformed fibers are observed in PBO and ultra high molecular weight polyethylene (e.g. Spectra) fabric armor systems.

Isotropic fibers (such as glass fibers, which are expected to fail in a manner more suitably characterized by, say, a distortion energy theory of failure) or other fibers that are brittle in lateral compression are expected to be inferior to fibers with similar mechanical properties that are fibrillar, or otherwise yield under lateral compression without disrupting the load-bearing elements of the fiber.

It has been shown that aramid fibers (such as Kevlar or Twaron) retain nearly all of their virgin fiber tensile strength following lateral compression. This is attributed to the microfibrillar structure of the fibers which apparently remains essentially undamaged at moderate to high levels of lateral strain (beyond the yield point). This characteristic of aramid fibers is more desirable than that of isotropic fibers such as glass or anisotropic (but otherwise brittle fibers) such as carbon fibers where yield in lateral compression is accompanied or closely followed by catastrophic failure.

That is not to say that the ultimate strength of fibrillar materials like Kevlar, Spectra or PBO is not affected by the presence of lateral stresses; rather, it may be more appropriate to say that they appear to be similarly affected, and affected to a lesser degree than more brittle fibers. The model over-predicts the performance of brittle fibers, accurately predicts the performance of aramids and PBO, and now is seen to under-predict the performance of M5.

This is consistent with the lack of a three dimensional failure model.

It is possible (since M5 fibers are expected to be stiffer and stronger than aramids or PBO fibers in lateral compression) that they retain a larger fraction of the one-dimensional tensile strength than either aramids or PBO when subjected to combined lateral compression and axial tension during the impact event. Examination of the failure of M5 yarns near the impact point suggests that they are indeed less affected by compressive loadings, as illustrated in Figure 10.

Another potential source of error in the dimensional analysis concerns the failure of the model to account for flaw isolation when fibers are incorporated into a matrix and tested under ballistic impact. That is, since the processing conditions used to produce the M5 fiber tested as part of this work were less than optimal, the flaw distribution in the fibers was larger than would be expected when the fiber is in full production. It was anticipated that processing of M5 into a composite would effectively isolate some of these flaws; some of the unexpected performance increase may be attributable to this flaw isolation. However, since the resin content of the composite was very low, and peak stresses during impact are quite localized around the impact point, flaw isolation was not expected to increase ballistic impact performance to the same degree that it was expected to increase strength or modulus.

7. SUMMARY

The ballistic impact performance of composite materials prepared from relatively inferior (3.9 GPa average ultimate tensile strength, 1.4% elongation at break, and 271 GPa initial modulus) M5 fiber was estimated using a dimensionless analysis model. These armor systems were estimated to perform at a level slightly inferior to aramid armor systems. However, M5 armor systems based on these fibers have been shown to provide performance almost as good as the best composite

materials ever prepared for fragmentation protection. Based on these results, it is estimated that fragmentation protective armor systems based on M5 will reduce the areal density of the ballistic component of these systems by approximately 40-60% over Kevlar KM2 fabric at the same level of protection.

REFERENCES

- Brew, B., Hine, P. J., and Ward, I. M., "The Properties of PIPD-Fibre/Epoxy Composites", *Composites Science and Technology*, Vol 59, No. 7, pp. 1109, 1999
- Cunniff, P. M., "Dimensionless Parameters for Optimization of Textile-Based Body Armor Systems", *Proceeding of the 18th International Symposium on Ballistics*, San Antonio, TX, Nov 1999
- Hageman, J. C. L., van der Horst, J. W., and De Groot, R. A., "An ab Initio Study of the Structural and Physical Properties of a Novel Rigid-Rod Polymer: PIPD", *Polymer*, Vol 40, No. 5, pp. 1313, 1999
- Klop, E. A., and Lammers, M., "XRD Study of the New Rigid-Rod Polymer Fibre PIPD", *Polymer*, Vol 39, No. 24, pp. 5987, 1998
- Lammers, M., Klop, E.A., Northolt, M.G. and Sikkema, D. J., "Mechanical Properties and Structural Transitions in the New Rigid-Rod Polymer Fibre PIPD ('M5') During the Manufacturing Process", *Polymer*, Vol 39, pp. 5999 1998
- Northolt, M.G. and Baltussen, J.J.M., "The Tensile and Compressive Deformation of Polymer and Carbon Fibers", *J. Appl. Poly Sci.* Vol 83, pp. 508-538, 2001
- Sikkema, D. J., "Design, Synthesis and Properties of a Novel Rigid Rod Polymer, PIPD or 'M5': High Modulus and Tenacity Fibres with Substantial Compressive Strength", *Polymer*, Vol 39, No. 24, pp. 5981, 1998
- Van der Jagt, O. C. and Beukers, A., "The Potential of a New Rigid-Rod Polymer Fibre ('M5') in Advanced Composite Structures", *Polymer*, Vol 40, pp. 1035, 1999